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CA 2373756 A1 2000/11/23

(21) **2 373 756**

(12) **DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION**

(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 2000/04/25
(87) Date publication PCT/PCT Publication Date: 2000/11/23
(85) Entrée phase nationale/National Entry: 2001/11/13
(86) N° demande PCT/PCT Application No.: EP 2000/003682
(87) N° publication PCT/PCT Publication No.: 2000/070694
(30) Priorité/Priority: 1999/05/15 (199 22 522.2) DE

(51) Cl.Int.⁷/Int.Cl.⁷ H01M 4/50, H01M 4/62, H01M 4/52,
H01M 10/40

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(54) Titre : PARTICULES A BASE D'OXYDES MIXTES ET DE LITHIUM, RECOUVERTES D'OXYDES METALLIQUES
(54) Title: COATED LITHIUM MIXED OXIDE PARTICLES

(57) Abrégé/Abstract:

The invention relates to lithium-mixed oxide particles coated with metal-oxide. Said particles are used to improve the characteristics of electrochemical cells. The invention relates to undoped and doped mixed oxides which are selected from the group $\text{Li}(\text{MnMe}_2)_2\text{O}_4$, $\text{Li}(\text{CoMe}_2)\text{O}_2$, $\text{Li}(\text{Ni}_{1-x-y}\text{Co}_x\text{Me}_y)\text{O}_2$ as cathode material. Me means at least one metal cation from the groups IIa, IIIa, IVa, IIb, IIIb, IVb, VIb, VIIb, VIII of the periodic table. Copper, silver, nickel, magnesium, zinc, aluminium, iron, cobalt, chromium, titanium and zircon are especially useful cations. Lithium is especially useful for the spinel compositions. The present invention also relates to lithium intercalations and insertion compounds that can be used for 4V-cathodes and have improved high temperature characteristics, especially at temperatures above room temperature. The invention further relates to the production and utilisation thereof, especially as cathode material in electrochemical cells. Various metal-oxides, especially oxides or mixed oxides of Zr, Al, Zn, Y, Ce, Sn, Ca, Si, Sr, Mg and Ti and the mixtures thereof, such as ZnO, CaO, SrO, SiO_2 , CaTiO_3 , MgAl_2O_4 , ZrO_2 , Al_2O_3 , Ce_2O_3 , Y_2O_3 , SnO_2 , TiO_2 and MgO for instance, can be used as coating materials. It has been found that the undesired reactions of the electrolyte with the electrode materials can be significantly hindered by means of the coating with said metal-oxides.

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(57) Abstract

The invention relates to lithium-mixed oxide particles coated with metal-oxide. Said particles are used to improve the characteristics of electrochemical cells. The invention relates to undoped and doped mixed oxides which are selected from the group $\text{Li}(\text{MnMe}_x)_2\text{O}_4$, $\text{Li}(\text{CoMe}_2)_2\text{O}_2$, $\text{Li}(\text{Ni}_{1-x-y}\text{Co}_x\text{Me}_y)_2\text{O}_2$ as cathode material. Me means at least one metal cation from the groups IIa, IIIa, IVa, IIb, IIIb, IVb, VIb, VIIb, VIII of the periodic table. Copper, silver, nickel, magnesium, zinc, aluminium, iron, cobalt, chromium, titanium and zircon are especially useful cations. Lithium is especially useful for the spinel compositions. The present invention also relates to lithium intercalations and insertion compounds that can be used for 4V-cathodes and have improved high temperature characteristics, especially at temperatures above room temperature. The invention further relates to the production and utilisation thereof, especially as cathode material in electrochemical cells. Various metal-oxides, especially oxides or mixed oxides of Zr, Al, Zn, Y, Ce, Sn, Ca, Si, Sr, Mg and Ti and the mixtures thereof, such as ZnO , CaO , SrO , SiO_2 , CaTiO_3 , MgAl_2O_4 , ZrO_2 , Al_2O_3 , Ce_2O_3 , Y_2O_3 , SnO_2 , TiO_2 and MgO for instance, can be used as coating materials. It has been found that the undesired reactions of the electrolyte with the electrode materials can be significantly hindered by means of the coating with said metal-oxides.

Coated lithium mixed oxide particles

The invention relates to coated lithium mixed oxide particles for improving the high-temperature properties of electrochemical cells.

5 The demand for rechargeable lithium batteries is high and will increase much more considerably still in the future. The reasons for this are the high energy density that can be achieved and the low weight of these batteries. These batteries are used in mobile telephones, portable
10 video cameras, laptops, etc.

As is known, the use of metallic lithium as anode material results, owing to dendrite formation during dissolution and deposition of the lithium, in inadequate cycle stability of the battery and in a considerable safety risk
15 (internal short-circuit) (J. Power Sources, 54 (1995) 151).

These problems have been solved by replacing the lithium-metal anode by other compounds which can reversibly intercalate lithium ions. The principle of functioning of lithium ion batteries is based on the fact that both the
20 cathode and anode materials can reversibly intercalate lithium ions, i.e. the lithium ions migrate out of the cathode during charging, diffuse through the electrolyte and are intercalated in the anode. During discharging, the same process occurs in the opposite direction. Owing to this
25 mechanism of functioning, these batteries are also referred to as "rocking-chair" or lithium ion batteries.

The resultant voltage of a cell of this type is determined by the lithium intercalation potentials of the electrodes. In order to achieve the highest possible
30 voltage, cathode materials which intercalate lithium ions at very high potentials and anode materials which intercalate

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lithium ions at very low potentials (vs. Li/Li^+) must be used. Cathode materials which satisfy these requirements are LiCoO_2 and LiNiO_2 , which have a layered structure, and LiMn_2O_4 , which has a cubic three-dimensional network structure. These
5 compounds deintercalate lithium ions at potentials of around 4 V (vs. Li/Li^+). In the case of the anode compounds, certain carbon compounds, such as, for example, graphite, meet the requirement of low potential and high capacity.

At the beginning of the 1990s, Sony brought a
10 lithium ion battery onto the market which consists of a lithium cobalt oxide cathode, a non-aqueous liquid electrolyte and a carbon anode (Progr. Batteries Solar Cells, 9 (1990) 20).

For 4 V cathodes, LiCoO_2 , LiNiO_2 and LiMn_2O_4 have
15 been discussed and employed. The electrolytes used are mixtures which contain aprotic solvents in addition to a conductive salt. The most frequently used solvents are ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl
20 carbonate (EMC). Although a whole series of conductive salts is being discussed, LiPF_6 is used virtually without exception. The anode used is generally graphite.

A disadvantage of the state-of-the-art batteries is that the high-temperature shelf life and cycle stability
25 are poor. The reasons for this, besides the electrolyte, are the cathode materials used, in particular lithium manganese spinel LiMn_2O_4 .

However, lithium manganese spinel is a very promising material as cathode for portable batteries. The
30 advantage over LiNiO_2 - and LiCoO_2 -based cathodes is improved safety in the charged state, the low toxicity and the lower costs of the raw materials.

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The disadvantages of the spinel are its low capacity and its inadequate high-temperature shelf life and consequently poor cycle stability at high temperatures. The reason for this is thought to be the solubility of divalent manganese in the electrolyte (Solid State Ionics 69 (1994) 59; J. Power Sources 66 (1997) 129; J. Electrochem. Soc. 144 (1997) 2178). The manganese in the spinel LiMn_2O_4 exists in two oxidation states, namely trivalent and tetravalent. The LiPF_6 -containing electrolyte always also contains water impurities. This water reacts with the LiPF_6 conductive salt to form LiF and acidic components, for example HF . These acidic components react with the trivalent manganese in the spinel to form Mn^{2+} and Mn^{4+} (disproportionation: $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$). This degradation does take place even at room temperature, but accelerates with increasing temperature.

One way of increasing the stability of the spinel at high temperatures is to dope it. For example, some of the manganese ions can be replaced by other, for example trivalent, metal cations. Antonini et al. report that spinels which have been doped with gallium and chromium (for example $\text{Li}_{1.02}\text{Ga}_{0.025}\text{Cr}_{0.025}\text{Mn}_{1.95}\text{O}_4$) exhibit a satisfactory shelf life and cycle stability at 55°C (J. Electrochem. Soc., 145 (1998) 2726).

A similar path is being trodden by the researchers at Bellcore Inc. They are replacing some of the manganese by aluminium and in addition some of the oxygen ions by fluoride ions ($(\text{Li}_{1-x}\text{Al}_y\text{Mn}_{2-x-y}\text{O}_{4-z}\text{F}_z)$). This doping likewise results in an improvement in the cycle stability at 55°C (WO 9856057).

Another possible solution is to modify the surface of the cathode material. US 5695887 proposes spinel cathodes

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which have a reduced surface area and whose catalytic centres are saturated by treatment with chelating agents, for example acetylacetone. Cathode materials of this type exhibit significantly reduced self-discharge and an improved shelf life at 55°C. The cycle stability at 55°C is only slightly improved (Solid State Ionics 104 (1997) 13).

Another possibility is to cover the cathode particles with a coating, for example a lithium borate glass (Solid State Ionics 104 (1997) 13). For this purpose, a spinel is introduced into a methanolic solution of H_3BO_3 , $LiBO_2 \cdot 8H_2O$ and $LiOH \cdot H_2O$ and the mixture is stirred at 50-80°C until the solvent has completely evaporated. The powder is subsequently heated to 600-800°C in order to ensure conversion into the borate. The shelf life at high temperatures is thereby improved. However, an improved cycle stability has not been found.

In WO 98/02930, undoped spinels are treated with alkali metal hydroxide solutions. The treated spinel is subsequently heated in a CO_2 atmosphere in order to convert the adherent hydroxides into the corresponding carbonates. The spinels modified in this way exhibit an improved high-temperature shelf life and improved cycle stability at high temperatures.

The coating of electrodes for improving various properties of lithium ion batteries has already been described a number of times.

For example, the cathode and/or anode are coated by pasting the active material together with binder and a conductive material onto the collector. A paste consisting of the coating material, binder and/or solvent is subsequently applied to the electrode. The coating materials mentioned are inorganic and/or organic materials,

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which may be conductive, for example Al_2O_3 , nickel, graphite, LiF , PVDF, etc. Lithium ion batteries which contain electrodes coated in this way exhibit high voltages and capacities and improved safety characteristics (EP 836238).

- 5 A very similar procedure is also followed in US 5869208. Here too, firstly the electrode paste (cathode material: lithium manganese spinel) is prepared and applied to the collector. The protective coating, consisting of a metal oxide and binder, is then pasted onto the electrode.
- 10 Examples of metal oxides used are aluminium oxide, titanium oxide and zirconium oxide.

 In JP 08236114, the electrode is likewise produced first, preferably $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ as active material, and then an oxide layer is applied by sputtering, vacuum vapour

15 deposition or CVD.

 In JP 09147916, a protective layer consisting of solid oxide particles, for example MgO , CaO , SrO , ZrO_2 , Al_2O_3 or SiO_2 , and a polymer, is applied to the side of the collector which contains the electrode. High voltages and

20 high cycle stability are thereby achieved.

 Another path is trodden in JP 09165984. The cathode material used is a lithium manganese spinel coated with boron oxide. This coating is generated during the spinel synthesis. To this end, a lithium, manganese and

25 boron compound is calcined in an oxidizing atmosphere. The boron oxide-coated spinels obtained in this way exhibit no manganese dissolution at high voltages.

 However, coatings are not only produced using oxidic materials, but also with polymers, as described in

30 JP 07296847 for improving the safety characteristics.

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In JP 08250120, the coating is carried out with sulfides, selenides and tellurides for improving the cycle performance, and in JP 08264183 with fluorides for improving the cycle life.

5 The object of the present invention is to provide electrode materials which do not have the disadvantages of the prior art and have an improved shelf life and cycle stability at high temperatures, in particular at temperatures above room temperature.

10 The object according to the invention is achieved by lithium mixed oxide particles which have been coated with one or more metal oxides.

 The invention also relates to a process for coating the lithium mixed oxide particles and to their use
15 in electrochemical cells, batteries and secondary lithium batteries.

 The present invention relates to undoped and doped mixed oxides as cathode materials, selected from the group consisting of $\text{Li}(\text{MnMe}_2)_2\text{O}_4$, $\text{Li}(\text{CoMe}_2)\text{O}_2$ and $\text{Li}(\text{Ni}_{1-x-y}\text{Co}_x\text{Me}_y)\text{O}_2$,
20 where Me is at least one metal cation from Groups IIa, IIIa, IVa, IIb, IIIb, IVb, VIb, VIIb and VIII of the Periodic Table of the Elements. Particularly suitable metal cations are copper, silver, nickel, magnesium, zinc, aluminium, iron, cobalt, chromium, titanium and zirconium, and also
25 lithium for the spinel compounds. The present invention likewise relates to other lithium intercalation and insertion compounds which are suitable for 4 V cathodes, having improved high-temperature properties, in particular at temperatures above room temperature, and to their
30 production and use, in particular as cathode material in electrochemical cells.

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In the present invention, the lithium mixed oxide particles are coated with metal oxides in order to achieve an improved shelf life and cycle stability at high temperatures (above room temperature).

5 Suitable coating materials are various metal oxides, in particular oxides or mixed oxides of Zr, Al, Zn, Y, Ce, Sn, Ca, Si, Sr, Mg and Ti, and mixtures thereof, for example ZnO, CaO, SrO, SiO₂, CaTiO₃, MgAl₂O₄, ZrO₂, Al₂O₃, Ce₂O₃, Y₂O₃, SnO₂, TiO₂ and MgO.

10 It has been found that the coating with said metal oxides enables the undesired reactions of the electrolyte with the electrode materials to be greatly inhibited.

 Surprisingly, it has been found that the coating of the lithium mixed oxide particles results in a
15 significant improvement in the high-temperature cycle stability of the cathodes produced therefrom. This results in a virtual halving of the capacity loss per cycle of the coated cathode material compared with uncoated cathode materials.

20 In addition, an improved shelf life above room temperature has been found. Spinel coated with metal oxides have significantly reduced manganese dissolution.

 It has furthermore been found that the coating of the individual particles has some advantages over coating of
25 the electrode bands. In the case of damage to the electrode material, the electrolyte can attack the majority of the active material in the case of coated bands, whereas these undesired reactions remain highly localized in the case of coating of the individual particles.

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The coating process allows layer thicknesses of from 0.03 μm to 5 μm to be achieved. Preferred layer thicknesses are from 0.05 μm to 3 μm . The lithium mixed oxide particles can have one or more coatings.

5 The coated lithium mixed oxide particles can be converted into 4 V cathodes for lithium ion batteries using the usual support materials and auxiliaries.

In addition, the coating is carried out by the supplier, which means that the battery manufacturer need not
10 carry out the process modifications necessary for coating.

Owing to the coating of the materials, an improvement in the safety aspects can also be expected.

The coating of the cathode material with inorganic materials greatly inhibits the undesired reactions of the
15 electrode material with the electrolyte and thus enables an improvement in the shelf life and cycle stability at elevated temperatures.

The cathode material according to the invention can be employed in secondary lithium ion batteries with
20 conventional electrolytes. Examples of suitable electrolytes are those with conductive salts selected from the group consisting of LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, and mixtures thereof. The electrolytes can also contain organic isocyanates
25 (DE 199 44 603) for reducing the water content. The electrolytes may also contain organic alkali metal salts (DE 199 10 968) as additive. Suitable alkali metal salts are alkali metal borates of the general formula



30 in which

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m and p are 0, 1, 2, 3 or 4, where $m + p = 4$, and R^1 and R^2 are identical or different,

5 are optionally bonded directly to one another via a single or double bond,

are each, individually or together, an aromatic or aliphatic carboxylic, dicarboxylic or sulfonic acid radical, or

10 are each, individually or together, an aromatic ring from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- or tetrasubstituted by A or Hal,
15 or

are each, individually or together, a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl and bipyridyl, which may be unsubstituted or
20 mono- to trisubstituted by A or Hal, or

are each, individually or together, an aromatic hydroxy acid from the group consisting of aromatic hydroxycarboxylic acids and aromatic hydroxysulfonic
25 acids, which may be unsubstituted or mono- to tetrasubstituted by A or Hal,

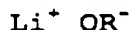
and

30 Hal is F, Cl or Br

and

A is alkyl having 1 to 6 carbon atoms, which may
35 be mono- to trihalogenated.

Likewise suitable are alkali metal alkoxides of the general formula



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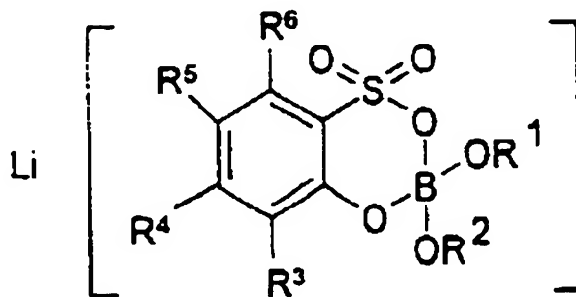
in which R

is an aromatic or aliphatic carboxylic, dicarboxylic or sulfonic acid radical, or

- 5 is an aromatic ring from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- to tetrasubstituted by A or Hal, or
- 10 is a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl and bipyridyl, which may be unsubstituted or mono- to trisubstituted by A or Hal, or
- 15 is an aromatic hydroxy acid from the group consisting of aromatic hydroxycarboxylic acids and aromatic hydroxysulfonic acids, which may be unsubstituted or mono- to tetrasubstituted by A or Hal,
- 20 and
- Hal is F, Cl or Br
- and
- 25 A is alkyl having 1 to 6 carbon atoms, which may be mono- to trihalogenated.

Lithium complex salts of the formula

30



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where

R¹ and R² are identical or different, are optionally directly bonded to one another via a single or double
5 bond, and are each, individually or together, an aromatic ring from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- to hexasubstituted by alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl or Br),
10

or are each, individually or together, an aromatic heterocyclic ring from the group consisting of pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or
15 mono- to tetrasubstituted by alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl or Br),

or are each, individually or together, an aromatic ring from the group consisting of hydroxybenzocarboxyl, hydroxynaphthalenecarboxyl, hydroxybenzosulfonyl and hydroxynaphthalenesulfonyl, which may be unsubstituted
20 or mono- to tetrasubstituted by alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl or Br),

25 R³ - R⁶ may each, individually or in pairs and optionally bonded directly to one another via a single or double bond, have the following meanings:

1. alkyl (C₁ to C₆), alkoxy (C₁ to C₆) or halogen (F, Cl or Br)
30

2. an aromatic ring from the groups consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which
35 may be unsubstituted or mono- to hexasubstituted by alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl or Br),

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pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl or Br),

5

which are prepared by the following process (DE 199 32 317):

10 a) chlorosulfonic acid is added to 3-, 4-, 5- or 6-substituted phenol in a suitable solvent,

b) the intermediate from a) is reacted with chlorotrimethylsilane, and the product is filtered and subjected to fractional distillation,

15

c) the intermediate from b) is reacted with lithium tetramethoxyborate(1-) in a suitable solvent, and the end product is isolated therefrom,

20 may also be present in the electrolyte.

The electrolytes may likewise comprise compounds of the following formula (DE 199 41 566):

25
$$[[[R^1(CR^2R^3)_k]_l A_x]_y Kt]^+ N(CF_3)_2^-$$

where

Kt = N, P, As, Sb, S or Se,

30

A = N, P, P(O), O, S, S(O), SO₂, As, As(O), Sb or Sb(O),

R¹, R² and R³

35

are identical or different

and are H, halogen, substituted and/or unsubstituted alkyl C_nH_{2n+1} , substituted and/or unsubstituted alkenyl

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having 1-18 carbon atoms and one or more double bonds,
 substituted and/or unsubstituted alkynyl having 1-18
 carbon atoms and one or more triple bonds, substituted
 and/or unsubstituted cycloalkyl C_mH_{2m-1} , mono- or
 5 polysubstituted and/or unsubstituted phenyl, substitu-
 ted and/or unsubstituted heteroaryl,

A can be included in R^1 , R^2 and/or R^3 in various
 positions,

10

Kt can be included in a cyclic or heterocyclic ring,

the groups bonded to Kt may be identical or different,

15 where

$n = 1-18$

$m = 3-7$

20

$k = 0$ or $1-6$

$l = 1$ or 2 in the case where $x = 1$ and 1 in the case
 where $x = 0$

25

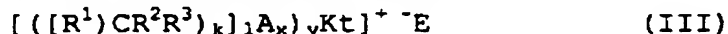
$x = 0$ or 1

$y = 1-4$.

30 The process for the preparation of these compounds is
 characterized in that an alkali metal salt of the
 general formula



where D^+ is selected from the group consisting of
 35 alkali metals, is reacted, in a polar organic solvent,
 with a salt of the general formula



where

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Kt, A, R¹, R², R³, k, l, x and y are as defined above,
and

5 E is F⁻, Cl⁻, Br⁻, I⁻, BF₄⁻, ClO₄⁻, AsF₆⁻, SbF₆⁻ or
PF₆⁻.

However, use can also be made of electrolytes
comprising compounds of the general formula (DE 199 53
10 638)



where

15 X is H, F, Cl, C_nF_{2n+1}, C_nF_{2n-1} or (SO₂)_kN(CR¹R²R³)₂,

Y is H, F or Cl

Z is H, F or Cl

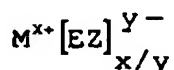
20 R¹, R² and R³ are H and/or alkyl, fluoroalkyl or cyclo-
alkyl

m is 0-9 and, if X = H, m ≠ 0

25 n is 1-9

k is 0 if m = 0 and k = 1 if m = 1-9,

30 prepared by reacting partially or perfluorinated
alkylsulfonyl fluorides with dimethylamine in organic
solvents, and complex salts of the general formula
(DE 199 51 804)



35

in which

x and y are 1, 2, 3, 4, 5 or 6

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M^{x+} is a metal ion

E is a Lewis acid selected from the group consisting
 5 of $BR^1R^2R^3$, $AlR^1R^2R^3$, $PR^1R^2R^3R^4R^5$, $AsR^1R^2R^3R^4R^5$ and
 $VR^1R^2R^3R^4R^5$,

R^1 to R^5 are identical or different, are optionally
 bonded directly to one another via a single or double
 10 bond, and each, individually or together, have the
 following meanings:

a halogen (F, Cl or Br),

15 an alkyl or alkoxy radical (C_1 to C_8), which can be
 partially or fully substituted by F, Cl or Br,

an aromatic ring, optionally bonded via oxygen, from
 the group consisting of phenyl, naphthyl, anthracenyl
 20 and phenanthrenyl, which may be unsubstituted or mono-
 to hexasubstituted by alkyl (C_1 to C_8) or F, Cl or Br,

an aromatic heterocyclic ring, optionally bonded via
 oxygen, from the group consisting of pyridyl, pyrazyl
 25 and pyrimidyl, which may be unsubstituted or mono- to
 tetrasubstituted by alkyl (C_1 to C_8) or F, Cl or Br, and

Z is OR^6 , NR^6R^7 , $CR^6R^7R^8$, OSO_2R^6 , $N(SO_2R^6)(SO_2R^7)$,
 30 $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$ or $OCOR^6$, where

R^6 to R^8 are identical or different, are optionally
 bonded directly to one another via a single or double
 bond and are each, individually or together,

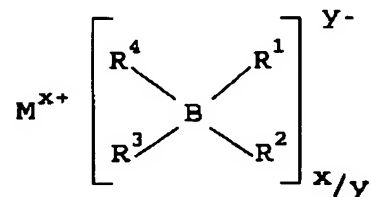
35 hydrogen or as defined for R^1 to R^5 ,

prepared by reacting a corresponding boron or
 phosphorus Lewis acid/solvent adduct with a lithium or
 tetraalkylammonium imide, methanide or triflate.

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It is also possible for borate salts (DE 199 59 722) of the general formula



5

in which

M is a metal ion or tetraalkylammonium,

x and y are 1, 2, 3, 4, 5 or 6,

10 R^1 to R^4 are identical or different and are alkoxy or carboxyl radicals (C_1-C_8), which are optionally bonded directly to one another via a single or double bond,

may be present. These borate salts are prepared by reacting a lithium tetraalkoxyborate or a 1:1 mixture of lithium alkoxide with a borate in an aprotic solvent with a suitable
15 hydroxyl or carboxyl compound in the ratio 2:1 or 4:1.

A general example of the invention is explained below.

Process for coating cathode materials

4 V cathode materials, in particular materials
20 having a layered structure (for example $Li(CoMe_2)O_2$ or $Li(Ni_{1-x-y}Co_xMe_y)O_2$) and spinels ($Li(MnMe_2)_2O_4$), are suspended in polar organic solvents, such as, for example, alcohols, aldehydes, halides or ketones, spinels also in water, and introduced into a reaction vessel. The materials can also
25 be suspended in non-polar organic solvents, such as, for example,

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cycloalkanes or aromatics. The reaction vessel is heatable and fitted with a stirrer. The reaction solution is warmed to temperatures between 10 and 100°C, depending on the boiling point of the solvent.

5

Suitable coating solutions are soluble metal salts selected from the group consisting of zirconium, aluminium, zinc, yttrium, cerium, tin, calcium, silicon, strontium, titanium and magnesium salts, and mixtures thereof, which are soluble in organic solvents or water. Suitable hydrolysis solutions are acids, bases or water, corresponding to the solvent used in the coating solution.

15 The coating solution and the hydrolysis solution are metered in slowly. The metering amounts and rates are dependent on the desired layer thicknesses and the metal salts employed. In order to ensure that the hydrolysis reaction proceeds quantitatively, the hydrolysis solution is added in excess.

25 When the reaction is complete, the solution is filtered, and the powder obtained is dried. In order to ensure complete conversion into the metal oxide, the dried powder must then be calcined. The powder is heated to from 400°C to 1000°C, preferably to from 700 to 850°C, and held at this temperature for from 10 minutes to 5 hours, preferred for from 20 to 60 minutes.

30

The particles can be given one or more coats. If desired, the first coating can be carried out with one metal oxide and the next coatings with oxides of other metals.

35

The examples below are intended to illustrate the invention in greater detail, but without representing a limitation.

EXAMPLESExample 1

Process for coating cathode materials with ZrO_2

100 g of lithium manganese spinel, SP30

- 5 Selectipur® from Merck, and 500 ml of ethanol, which serves as solvent, are introduced into a 2 litre flask. This flask dips into a water bath and is provided with a stirrer. The water bath is heated to 40°C.

- The coating solution used is tetrapropyl
10 orthozirconate (26.58 g) dissolved in ethanol (521.8 ml). The hydrolysis solution used is water (14.66 g). The two solutions are metered in slowly. The zirconium propylate addition is complete after about 6.5 hours. In order to ensure that the hydrolysis reaction also proceeds
15 quantitatively, water (36.4 g) is added for a further 16.2 hours for post-hydrolysis.

- When the reaction is complete, the ethanolic solution is filtered, and the resultant powder is dried at about 100°C. In order to ensure complete conversion into
20 ZrO_2 , the dried powder must then be calcined. After drying, powder is therefore heated to 800°C and held at this temperature for 30 minutes.

Example 2

Storage test at elevated temperatures

- 25 Commercially available spinel cathode powder, SP30 and SP35 Selectipur® from Merck, is employed. The samples, untreated SP30 and ZrO_2 -coated SP30, are in each case introduced into a 1 litre aluminium bottle (about 3 g of sample), and 30 ml of electrolyte are added (LP600
30 Selectipur® from Merck, EC:DEC:PC 2:1:3 1M LiPF_6). The aluminium bottles are subsequently sealed in a gas-tight

manner. These preparations are all carried out in an argon-flushed glove box. The bottles prepared in this way are then removed from glove box via the lock and stored in a drying cabinet at 80°C for 6 or 13 days. When the storage
5 test is complete, the aluminium bottles are cooled to room temperature and introduced into the glove box again via the lock and opened therein. The electrolyte is filtered, and the amount of manganese dissolved in the electrolyte is determined quantitatively by means of ICP-OES.

10 Table 1 compares the analytical results for the uncoated and coated lithium manganese spinels.

	SP30 uncoated	SP30 coated with ZrO ₂
Room temperature, 15 days	5 ppm	3 ppm
80°C, 6 days	220 ppm	100 ppm
80°C, 13 days	460 ppm	140 ppm

Table 1: Results of the manganese determination

The manganese dissolution in the case of the uncoated spinels is very considerable and increases further
15 with time. In the case of the coated spinels, by contrast, the manganese dissolution is significantly reduced both in absolute figures and also as a function of the storage time. The significant improvement in the high-temperature shelf life owing to the metal oxide coating is clearly evident for
20 these cathode materials.

Example 3

Cycling at high-temperatures

The coated cathode powder prepared as described in Example 1 and, as comparison, an uncoated material SP30
25 Selectipur® from Merck are cycled at 60°C.

In order to produce the electrodes, the cathode powder is mixed well with 15% of conductive black and 5% of PVDF (binder material). The paste prepared in this way is applied to an aluminium mesh serving as collector and dried overnight at 175°C under an argon atmosphere and under reduced pressure. The dried electrode is introduced into the argon-flushed glove box via the lock and installed in the measurement cell. The counterelectrode and reference electrode are lithium metal. The electrolyte used is LP50 Selectipur® from Merck (1M LiPF₆ in EC:EMC 50:50% by weight). The measurement cell with the electrodes and the electrolyte is placed in a steel container, which is sealed in a gas-tight manner. The cell produced in this way is removed from the glove box via the lock and placed in a climate-controlled cabinet set to 60°C. After the measurement cell has been connected to a potentiostat/galvanostat, the electrode is cycled (charging for 5 hours, discharging for 5 hours).

The result is that the cycle stability of the uncoated spinel is lower than that of the coated spinel.

In the first 5 cycles, irreversible reactions take place, such as, for example, film formation on the cathode and anode, meaning that they cannot be employed for the calculation. The loss in capacity per cycle of the uncoated spinel is then 0.78 mAh/g, while the ZrO₂-coated spinel only loses 0.45 mAh/g per cycle. This is a virtual halving of the loss in capacity per cycle. This shows that the high-temperature cycle stability of the cathode powder is significantly improved by coating with oxides.

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CLAIMS:

1. Lithium mixed oxide particles, characterized in that the particles are selected from the group consisting of $\text{Li}(\text{MnMe}_2)_2\text{O}_4$ and other lithium intercalation and insertion compounds and that the particles have been simply or multiply coated with metal oxides selected from the group consisting of ZnO , CaO , SrO , SiO_2 , CaTiO_3 , MgAl_2O_4 , ZrO_2 , Al_2O_3 , Ce_2O_3 , Y_2O_3 , SnO_2 , TiO_2 and MgO .
2. Lithium mixed oxide particles according to claim 1, characterized in that the layer thicknesses of the metal oxides are $0.05\text{-}3\text{ }\mu\text{m}$.
3. Cathodes essentially consisting of lithium mixed oxide particles according to one of claims 1 and 2 and conventional support materials and auxiliaries.
4. Process for the preparation of lithium mixed oxide particles coated with one or more metal oxides according to claim 1, characterized in that the particles are suspended in an organic solvent, the suspension is mixed with a solution of a hydrolyzable metal compound and a hydrolysis solution, and the coated particles are then filtered off, dried and optionally calcined.
5. Process for the preparation of lithium mixed oxide particles coated with one or more metal oxides according to claim 4, characterized in that the metal oxides are selected from the group consisting of ZnO , CaO , SrO , SiO_2 , CaTiO_3 , MgAl_2O_4 , ZrO_2 , Al_2O_3 , Ce_2O_3 , Y_2O_3 , SnO_2 , TiO_2 and MgO .
6. Process for the preparation of lithium mixed oxide particles coated with one or more metal oxides according to claim 4, characterized in that the hydrolysis solution is an acid, a base or water.

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7. Use of coated lithium mixed oxide particles according to any one of claims 1 to 3 for the production of cathodes having an improved shelf life and cycle stability at temperatures above room temperature.
- 5 8. Use of coated lithium mixed oxide particles according to any one of claims 1 to 3 for the production of 4 V cathodes.
9. Use of coated lithium mixed oxide particles according to any one of claims 1 to 3 in electrodes for
10 electrochemical cells, batteries and secondary lithium batteries.

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